# Extension of the Andrade Equation for Viscosity at the Normal Melting Point

JOHN M. MATSEN[1] and ERNEST F. JOHNSON
Department of Chemical Engineering, Princeton University, Princeton, N. J.

OF THE MANY attempts to express liquid viscosity as a simple function of molecular structure, none is more basic than Andrade's equation for melting point viscosity (*1*), and in the region for which Andrade's theory was developed few theories have been more successful.

Andrade regards the liquid state as similar to the solid state, except that binding forces have been relaxed. Thus, at the melting point, the molecule vibrates much as it does in the solid, but its equilibrium position will move slowly. At this temperature momentum is shared between the vibrating molecules in adjacent layers at each extreme libration of oscillation. Assuming that one third of the molecules are vibrating along each axis, Andrade obtains the following formula for melting point viscosity:

$$\eta = \frac{4}{3}\,\frac{\nu m}{\sigma} \qquad (1)$$

where

$\eta$ = viscosity
$\nu$ = frequency of vibration
$m$ = mass of molecule
$\sigma$ = average distance of separation

The frequency of simple molecules may be approximated by the Lindemann formula (*6*):

$$\nu = C\left(\frac{T}{V^{2/3}M}\right)^{1/2} \qquad (2)$$

where

$c$ = constant, $2.8 \times 10^{12}$ (in c.g.s. units)
T = absolute temperature, ° K.
$V$ = molar volume, cubic centimeter per mole
$M$ = molecular weight

Thus at the melting point:

$$\eta = 5.1 \times 10^{-4}\,(MT)^{1/2}/V^{2/3} \qquad (3)$$

or

$$\eta = 5.1 \times 10^{-4}\rho^{2/3}T^{1/2}/M^{1/6} \qquad (4)$$

where $\rho$ = density, grams per cubic cenitimeter.

This equation involves several restrictive assumptions. Both the liquid and the solid should be essentially cubic in structure, and there should be little volume change upon melting. The molecules must be symmetrical and cannot themselves consist of vibrating systems of atoms. For the alkali metals and the alkali halides these assumptions are reasonable, and the equation agrees remarkably well with empirical data. A constant of $5.56 \times 10^{-4}$ gives the best agreement.

In order to extend this equation Andrade has suggested that a proportionality constant $\beta$ be substituted to give:

$$\eta = \beta\rho^{2/3}T^{1/2}/M^{1/6} \qquad (5)$$

Properties of $\beta$, which is a characteristic of the molecule have been predicted:

1. The smallest value of $\beta$, $5.1 \times 10^{-4}$, will occur for simple, symmetrical monatomic liquids.
2. For molecules of similar structure $\beta$ will remain essentially constant.
3. In a homologous series $\beta$ will increase regularly with increases in chain length.
4. As a molecule departs from central symmetry, $\beta$ will increase rapidly.

Andrade has calculated $\beta$ for several compounds in support of these predictions, but many additional data on $\beta$ are needed for proper testing.

This article presents a number of newly determined values of $\beta$ and discusses their agreement with predicted behavior. Melting point values of viscosity and density were obtained by extrapolation of data given by Landolt-Börnstein (*5*), Rossini (*8*), Andrade (*2*), Dreisbach (*3*), and Griffing (*4*). Equation 5 was rearranged to solve for $\beta$. The anomalous results are presented in Table I and are discussed below. Figure 1 shows the variations of $\beta$ with chain length for several hydrocarbon series.

### HYDROGEN CYANIDE

A value of $3.61 \times 10^{-4}$ was obtained for the $\beta$ of hydrogen cyanide. This is well below the theoretical minimum value of $5.1 \times 10^{-4}$ and is even further below the average experimental value of $5.56 \times 10^{-4}$ for the ideal, monatomic liquids. Since hydrogen cyanide is triatomic and highly unsymmetrical, a much higher value of $\beta$ would be predicted. This is the only compound yet investigated which exhibits such behavior, and no explanation can be offered at present.

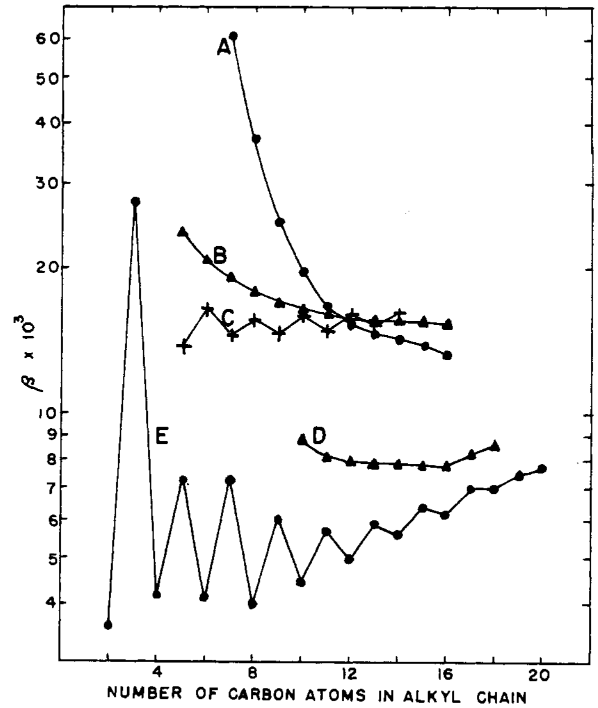

Figure 1. Effect of chain length on $\beta$

A. n-Alkylbenzenes
B. n-Alkylcyclohexanes
C. *n*-Alkylcyclopentanes
D. 1-Alkenes
E. *n*-Alkanes

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[1] Present address, Department of Chemical Engineering, Columbia University, New York 27, N. Y.

## METHANE AND SIMILAR COMPOUNDS

Andrade (2) calculated $\beta$ to be $20.1 \times 10^{-4}$ for methane. This is close to his values for carbon tetrachloride and silicon tetrachloride, given in Table I, and would support the hypothesis that $\beta$ will remain essentially constant for compounds of similar structure. He apparently made an error, and the present study found $\beta$ to be $5.80 \times 10^{-4}$, indicating that methane in viscous flow is more akin to the monatomic liquids than to structurally similar compounds. Such a result could be deduced from a knowledge of structural properties. The methane molecule is smaller and more nearly spherical than the tetrahedral carbon tetrachloride and silicon tetrachloride molecules. The bond lengths are shorter, and the light hydrogen atoms exert a much smaller bending moment on these bonds. Hence methane is a much more rigid molecule than carbon tetrachloride or silicon tetrachloride and being small, spherical, and rigid it would behave more like the ideal simple liquids.

## *n*-ALKANES

For the normal paraffins $\beta$ does not increase regularly with chain length as expected but alternates, being greater for members of the series which have an odd number of carbon atoms. This alternation is probably due to the presence of two liquid and three solid configurations as explained by Mumford (7). The liquids above $C_{16}$ have the

Table I. Properties of Liquids at Their Melting Points

| Formula | $\eta$, Poise × 100$^a$ | $M$ | T, ° K. | $\rho$, G./Cc. | $\beta \times 10^3$ |
|---|---|---|---|---|---|
| | Hydrogen Cyanide | | | | |
| HCN | 0.274 (5) | 27 | 259 | 0.736 | 0.361 |
| | Methane and Similar Compounds | | | | |
| $CH_4$ | 0.205 | 16 | 90.7 | 0.453 | 0.580 |
| $CCl_4$ | 19.8 (2) | 153.8 | 250 | 1.68 | 2.05 |
| $SiCl_4$ | 15.3 (2) | 170.1 | 184 | 1.73 | 1.85 |
| | *n*-Alkanes | | | | |
| $C_2H_6$ | 1.44 | 30 | 89.9 | 0.657 | 3.58 |
| $C_3H_8$ | 11.1 | 44 | 85.5 | 0.730 | 27.8 |
| $C_4H_{10}$ | 2.01 | 58 | 134.8 | 0.738 | 4.17 |
| $C_5H_{12}$ | 3.56 | 72 | 143.3 | 0.762 | 7.29 |
| $C_6H_{14}$ | 2.17 | 86 | 177.8 | 0.758 | 4.11 |
| $C_7H_{16}$ | 3.85 | 100 | 182.6 | 0.774 | 7.27 |
| $C_8H_{18}$ | 2.22 | 114 | 216.4 | 0.764 | 3.97 |
| $C_9H_{20}$ | 3.34 | 128 | 219.6 | 0.775 | 6.01 |
| $C_{10}H_{22}$ | 2.52 | 142 | 243.5 | 0.768 | 4.45 |
| $C_{11}H_{24}$ | 3.25 | 156 | 247.6 | 0.774 | 5.68 |
| $C_{12}H_{26}$ | 2.87 | 170 | 263.6 | 0.771 | 4.95 |
| $C_{13}H_{28}$ | 3.40 | 184 | 267.8 | 0.775 | 5.89 |
| $C_{14}H_{30}$ | 3.26 | 198 | 279.0 | 0.772 | 5.60 |
| $C_{15}H_{32}$ | 3.69 | 212 | 283.1 | 0.776 | 6.36 |
| $C_{16}H_{34}$ | 3.62 | 226 | 291.3 | 0.775 | 6.20 |
| $C_{17}H_{36}$ | 4.01 | 240 | 295.1 | 0.777 | 6.98 |
| $C_{18}H_{38}$ | 4.09 | 254 | 301.3 | 0.776 | 7.01 |
| $C_{19}H_{40}$ | 4.35 | 268 | 305.3 | 0.777 | 7.47 |
| $C_{20}H_{42}$ | 4.50 | 282 | 310.0 | 0.777 | 7.74 |
| | *n*-Alkylcyclopentanes | | | | |
| $C_{12}H_{24}$ | 7.88 | 168 | 220.0 | 0.857 | 13.8 |
| $C_{13}H_{26}$ | 9.36 | 182 | 229.2 | 0.846 | 16.5 |
| $C_{14}H_{28}$ | 8.39 | 196 | 244.2 | 0.843 | 14.5 |
| $C_{15}H_{30}$ | 9.06 | 210 | 251.0 | 0.842 | 15.6 |
| $C_{16}H_{32}$ | 8.56 | 224 | 263.2 | 0.835 | 14.7 |
| $C_{17}H_{34}$ | 9.31 | 238 | 268.2 | 0.835 | 16.0 |
| $C_{18}H_{36}$ | 8.80 | 252 | 278.2 | 0.832 | 14.9 |
| $C_{19}H_{38}$ | 9.44 | 266 | 282.2 | 0.829 | 16.0 |
| $C_{20}H_{40}$ | 8.99 | 280 | 290.2 | 0.826 | 15.3 |
| $C_{21}H_{42}$ | 9.50 | 294 | 294.2 | 0.825 | 16.2 |
| | 1-Alkenes | | | | |
| $C_2H_4$ | 0.685 | 28 | 103.8 | 0.658 | 1.56 |
| $C_3H_6$ | 15.3 | 42 | 88.0 | 0.770 | 36.3 |
| $C_{12}H_{24}$ | 4.91 | 168 | 237.9 | 0.783 | 8.81 |
| $C_{13}H_{26}$ | 4.57 | 182 | 250.1 | 0.790 | 8.05 |
| $C_{14}H_{28}$ | 4.58 | 196 | 260.3 | 0.795 | 7.96 |
| $C_{15}H_{30}$ | 4.54 | 210 | 269.4 | 0.793 | 7.87 |
| $C_{16}H_{32}$ | 4.55 | 224 | 277.3 | 0.792 | 7.84 |
| $C_{17}H_{34}$ | 4.51 | 238 | 284.4 | 0.791 | 7.80 |
| $C_{18}H_{36}$ | 4.53 | 252 | 290.8 | 0.791 | 7.79 |
| $C_{19}H_{38}$ | 4.30 | 266 | 296.6 | 0.790 | 8.26 |
| $C_{20}H_{40}$ | 4.94 | 280 | 301.8 | 0.789 | 8.54 |
| | *n*-Alkylbenzenes | | | | |
| $C_6H_6$ | 0.814 | 78 | 278.7 | 0.874 | 1.11 |
| $C_{13}H_{20}$ | 36.1 | 176 | 225.2 | 0.909 | 60.6 |

| Formula | $\eta$, Poise × 10$^a$ | $M$ | T, ° K. | $\rho$, G./Cc. | $\beta \times 10^3$ |
|---|---|---|---|---|---|
| $C_{14}H_{22}$ | 22.7 | 190 | 247.2 | 0.896 | 37.3 |
| $C_{15}H_{24}$ | 14.9 | 204 | 249.2 | 0.888 | 24.9 |
| $C_{16}H_{26}$ | 11.9 | 218 | 258.8 | 0.880 | 19.7 |
| $C_{17}H_{28}$ | 10.1 | 232 | 268.2 | 0.875 | 16.8 |
| $C_{18}H_{30}$ | 9.31 | 246 | 276.2 | 0.869 | 15.4 |
| $C_{19}H_{32}$ | 8.84 | 260 | 283.2 | 0.862 | 14.7 |
| $C_{20}H_{34}$ | 8.64 | 274 | 289.2 | 0.858 | 14.3 |
| $C_{21}H_{36}$ | 8.39 | 288 | 295.2 | 0.854 | 13.9 |
| $C_{22}H_{38}$ | 7.90 | 302 | 300.2 | 0.849 | 13.2 |
| | *n*-Alkylcyclohexanes | | | | |
| $C_{11}H_{22}$ | 13.5 | 154 | 215.7 | 0.864 | 23.5 |
| $C_{12}H_{24}$ | 12.1 | 168 | 230.2 | 0.852 | 20.8 |
| $C_{13}H_{26}$ | 11.2 | 182 | 242.6 | 0.847 | 19.1 |
| $C_{14}H_{28}$ | 10.35 | 196 | 253.5 | 0.843 | 17.6 |
| $C_{15}H_{30}$ | 9.92 | 210 | 263.0 | 0.838 | 16.8 |
| $C_{16}H_{32}$ | 9.70 | 224 | 271.4 | 0.835 | 16.3 |
| $C_{17}H_{34}$ | 9.53 | 238 | 279.0 | 0.833 | 16.0 |
| $C_{18}H_{36}$ | 9.41 | 252 | 285.7 | 0.829 | 15.9 |
| $C_{19}H_{38}$ | 9.24 | 266 | 291.7 | 0.826 | 15.6 |
| $C_{20}H_{40}$ | 9.21 | 280 | 297.2 | 0.825 | 15.6 |
| $C_{21}H_{42}$ | 9.20 | 294 | 302.2 | 0.822 | 15.5 |
| $C_{22}H_{44}$ | 9.12 | 308 | 306.8 | 0.820 | 15.4 |
| | Disubstituted Benzenes | | | | |
| *o*-$C_6H_4(CH_3)_2$ | 1.79 | 106 | 248.0 | 0.918 | 2.63 |
| *m*- | 1.82 | 106 | 225.3 | 0.921 | 2.79 |
| *p*- | 0.704 | 106 | 286.4 | 0.867 | 0.995 |
| *o*-$C_6H_4CH_3Cl$ | 2.73 (3) | 126.5 | 239.2 | 1.14 | 3.17 |
| *m*- | 3.04 (5) | 126.5 | 225.4 | 1.14 | 4.15 |
| *p*- | 1.06 (5) | 126.5 | 280.7 | 1.07 | 1.35 |
| *o*-$C_6H_4CH_3Br$ | 3.29 (3) | 171 | 246.2 | 1.48 | 3.80 |
| *m*- | 4.01 (5) | 171 | 233.4 | 1.48 | 4.76 |
| *p*- | 1.14 (3) | 171 | 301.2 | 1.39 | 1.24 |
| *o*-$C_6H_4CH_3NO_2$ | 2.54 (5) | 137 | 270.0 | 1.19 | 3.13 |
| *m*- | 2.54 (5) | 137 | 288.7 | 1.16 | 2.92 |
| *p*- | 1.36 (5) | 137 | 324.5 | 1.24 | 1.63 |
| *o*-$C_6H_4CH_3OH$ | 5.97 (3) | 108 | 304.0 | 1.04 | 6.97 |
| *m*- | 37.1 (3) | 108 | 284.9 | 1.05 | 45.5 |
| *p*- | 8.67 (3) | 108 | 307.7 | 1.02 | 10.6 |
| *o*-$C_6H_4CH_3NH_2$ | 24.8 (3) | 107 | 256.9 | 1.03 | 32.9 |
| *p*- | 1.95 (3) | 107 | 316.9 | 1.07 | 2.29 |
| *o*-$C_6H_4NH_2F$ | 10.1 (5) | 112 | 244.0 | 1.19 | 12.6 |
| *p*- | 5.29 (5) | 112 | 272.4 | 1.19 | 6.45 |
| *o*-$C_6H_4NH_2Cl$ | 6.45 (3) | 127.6 | 271.2 | 1.23 | 7.61 |
| *m*- | 10.3 (3) | 127.6 | 262.9 | 1.24 | 12.3 |
| *o*-$C_6H_4NH_2Br$ | 3.90 (5) | 172 | 304.2 | 1.56 | 3.93 |
| *m*- | 7.60 (5) | 172 | 290.0 | 1.58 | 7.83 |
| *p*- | 2.27 (5) | 172 | 339.5 | 1.56 | 2.16 |
| *o*-$C_6H_4NO_2F$ | 4.97 (5) | 141 | 267.2 | 1.31 | 5.86 |
| *m*- | 3.50 (5) | 141 | 276.8 | 1.31 | 4.06 |
| *p*- | 2.44 (5) | 141 | 300.2 | 1.32 | 2.70 |
| *o*-$C_6H_4NO_2Cl$ | 2.64 (5) | 157.5 | 305.7 | 1.36 | 2.86 |
| *p*- | 1.47 (5) | 157.5 | 356.6 | 1.45 | 1.41 |
| *o*-$C_6H_4ClOH$ | 7.50 (4) | 128.5 | 281.9 | 1.26 | 8.61 |
| *p*- | 6.96 (4) | 128.5 | 316.2 | 1.26 | 7.55 |
| *o*-$C_6H_4Cl_2$ | 2.85 (4) | 147 | 256.1 | 1.36 | 3.34 |
| *m*- | 2.63 (4) | 147 | 248.4 | 1.34 | 3.16 |
| *p*- | 0.865 (4) | 147 | 326.2 | 1.25 | 0.946 |

[a] Source of viscosity data is (8), unless otherwise noted.

so-called alpha configuration of rigid, rotating, planar, zigzag chains. They tend to crystallize initially in this form with the chains perpendicular to the terminal planes of the crystal. Below $C_{16}$ the liquid molecules assume the beta configuration, a helix which uncoils upon crystallization to give planar, zigzag chains which are tilted with respect to the terminal planes of the crystal. In beta crystals of odd-numbered chains the distances between adjacent terminal planes vary, the crystal will be less stable than one with an even number of carbon atoms in its molecules, and it will have a lower melting point. Alkane melting points are shown in Figure 2. A given alkane will crystallize in the same configuration which it has in the liquid, but if a higher-melting configuration exists, the substance will slowly change to that form.

Viscosity and hence $\beta$ are inversely dependent on temperature. Thus, the differences in melting points of odd and even members of the alkane series explain the alternation of $\beta$. The extremely high $\beta$ of propane is attributed to the fact that this molecule is highly unsymmetrical.

## *n*-ALKYLCYCLOPENTANES

In the alkylcyclopentanes as in the alkanes, $\beta$ alternates with chain length. Two melting point curves are observed in Figure 2, and the alternation of $\beta$ is attributed to the same effect of crystal structure as exists in the alkanes, although crystal data on the alkylcyclopentanes are not available.

The cyclopentane group is relatively large and heavy and cannot lie in the same plane as the alkyl chain. Asymmetry and general resistance to flow are thus increased, and $\beta$ is considerably greater than for the alkanes.

## 1-ALKENES

No alternation of $\beta$ is apparent in the case of the 1-alkenes, indicating that in a given region, only a single crystal form is present. The sharp increase of $\beta$ above $C_{18}$ may indicate the presence of another crystal form for the higher members of the series.

## *n*-ALKYLBENZENES AND *n*-ALKYLCYCLOHEXANES

In the alkylbenzene and alkylcyclohexane series, $\beta$ decreases steadily with increase in chain length, contrary to expected behavior. $\beta$ is considerably lower for the simple alkanes than for alkanes to which another group has been added, probably because the added group decreases symmetry and increases resistance to flow. As the alkyl chain becomes longer, the relative effect of a single substitution becomes less, however, and $\beta$ approaches the limiting value of the alkane.

The fact that $\beta$ does not decrease in the alkylcyclopentane series would seem to contradict this explanation.

## DISUBSTITUTED BENZENES

Andrade has stated that $\beta$ will increase rapidly as a molecule departs from central symmetry. To investigate this more thoroughly $\beta$ was calculated for the isomers of 13 disubstituted benzenes. These data show $\beta$ to be least for the para isomers and generally greatest for the meta isomers. This may be simply a function of the relative melting points, as postulated for the *n*-alkanes.

It is idle to say that $\beta$ will increase rapidly with departure from central symmetry, if there is no measure of such symmetry. It was first thought that the dipole moment might be such a yardstick and might have a significant effect of $\beta$, because such a moment would tend to limit the rotational and translational freedom of the molecule and provide an additional mechanism for momentum transfer. No useful relationship could be found. Depending on the nature of the two substituents on the benzene ring, the dipole moment is either greatest or least for the para isomer. The moment always assumes an intermediate value for the meta isomer. On the other hand $\beta$ is always least for para isomers and is usually greatest for meta isomers.

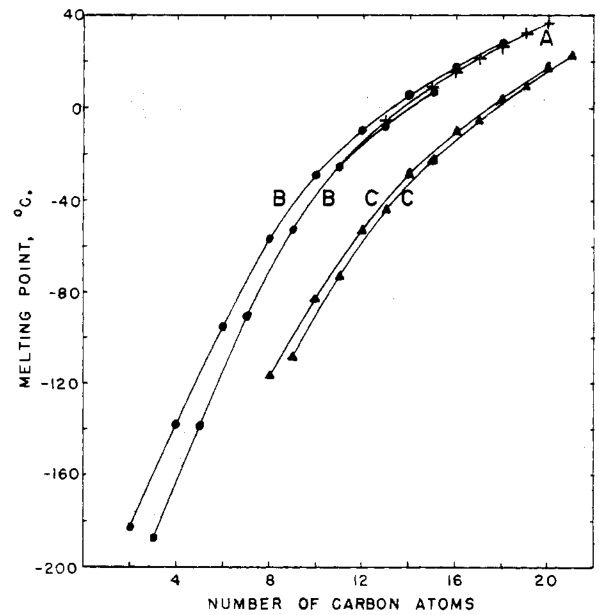

Figure 2. Alternation of melting points with chain length

A. *n*-Alkanes, alpha configuration
B. *n*-Alkanes, beta configuration
C. *n*-Alkylcyclopentanes

The third moment about the mean is used as a statistical test of symmetry, being zero for a perfectly symmetrical distribution. For a molecule, the third moment is defined as $\sum \vec{r}_i^{\,3} m_i$ where $\vec{r}_i$ is the vector distance of an atom from the center of mass of the molecule and $m_i$ is its mass. No correlation was found between the third moment and $\beta$.

With such a limited number of cases studied, it is difficult to make generalization concerning the effect of different substituent groups on $\beta$. Anilines have larger $\beta$'s than toluenes. Considering the halogens, however, $\beta$'s for chlorotoluenes are smaller than for bromotoluenes, but are larger for chloroanilines than for bromoanilines.

## CONCLUSIONS

For some of the series discussed above, the behavior of $\beta$ has been explained within the limits of the Andrade theory. Investigation of additional members of such series will undoubtedly shed more light on the accuracy of these explanations. In other cases, however, such rationalizations have been insufficient, and $\beta$ seems to have no significance. Andrade's equation is useful for the simple liquids, but the validity of extending it to more complex molecules by means of $\beta$ seems questionable.

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